



Comparative assessment of Reactive Black 5 removal from aqueous solution using organically modified montmorillonite clays

Sabiha Hakkar^{1,2} · Abdecharif Boumaza¹ · Mounir Mekidiche³ · Imen Amri^{4,5,7} · Kawther Yahya⁵ · Roufaida Merir⁶ · Khaled Hosni⁷ · Besma Mellah⁷ · Nouredine Hamdi^{5,7}

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Abstract

The discharge of synthetic dyes such as Reactive Black 5 (RB5) into aquatic environments poses a serious environmental challenge due to their persistence, toxicity, and resistance to conventional wastewater treatments. In this study, organoclays were synthesized by modifying natural montmorillonite clays originating from Algeria (Mnt A) and Germany (Mnt G) using hexadecyltrimethylammonium bromide (HDTMA) and hydrochloric acid (HCl), aiming to enhance their adsorption efficiency for RB5 removal. The clays were characterized using granulometry, XRD, FTIR, TGA-DTG, XRF, and zeta potential analysis, confirming successful modification. Batch adsorption experiments showed rapid dye removal within 60 min, with optimal performance at pH 2, an initial dye concentration of 100 mg/L. Kinetic modeling revealed that the adsorption process followed a pseudo-second-order model, while the equilibrium data were fitted to Langmuir, Freundlich, and Temkin isotherm models. Among these, Langmuir provided the best fit, indicating monolayer chemisorption, with Mnt AM exhibiting the highest adsorption capacity (113.4 mg/g) compared to Mnt GM (101.8 mg/g) and the raw montmorillonite. Temkin model analysis further contributed to understanding the energy distribution and adsorbent–adsorbate interactions. Mechanistic insights indicated that the unmodified clays relied mainly on cation bridging, hydrogen bonding, and van der Waals forces, while HDTMA-modified clays benefited from the additional electrostatic attraction, the hydrophobic effects, and π – π stacking. These results underscore the potential of organoclays as efficient, reusable adsorbents for textile wastewater remediation.

Keywords Montmorillonite · Adsorption mechanism · Organoclay · Wastewater treatment · Reactive Black 5

Responsible Editor: Ridha Djellabi.

✉ Imen Amri
imen.amri@uevora.pt; imen.amri@cnrsm.rnrt.tn

✉ Nouredine Hamdi
Nouredine.Hamdi@isstegb.mu.tn; nouryhamdi@gmail.com

¹ Laboratory of Structures, Properties and Interatomic Interactions (LASPI2A), Department of Science of Matter, Abbes Laghrour University, 40000 Khenchela, Algeria

² Laboratory of Engineering and Sciences of Advanced Materials (ISMA), Abbes Laghrour-University, PO 1252, 40004 Khenchela, Algeria

³ Laboratory of Catalysis and Synthesis in Organic Chemistry, Department of Chemistry, University of Tlemcen, 13000 Tlemcen, Algeria

⁴ Renewable Energies Chair, Polo da Mitra da Universidade de Évora, Nossa Senhora da Tourega, 7000-083 Évora, Portugal

⁵ Higher Institute of Water Sciences and Techniques, University of Gabes, 6072 Zrig, Tunisia

⁶ Laboratory of Multiphasic Polymeric Materials, Department of Process Engineering, Faculty of Technology, Ferhat Abbas Sétif 1 University, 19000 Setif, Algeria

⁷ Laboratory of Composite Materials and Clay Minerals, National Center for Research in Material Sciences (CNRSM), 8020 Soliman, Bordj Cedria, Tunisia

Introduction

Freshwater need has increased as a result of the world's population increase, urbanization, industrialization, and the careless use of natural water resources. Since freshwater supplies are few, and the world's population is predicted to reach 10 billion people by 2050, the 1 billion people who do not now have access to safe drinking water may rise. (Kapoor et al. 2022). The occurrence of extremely harmful compounds in wastewater is one of the main environmental issues associated with this pollution (Tsoutsas et al. 2023). About 20% of all water pollution worldwide is caused by the textile sector, which is a major contributor. The main causes of this pollution are the dyeing, finishing, and washing of synthetic garments, all of them discharge toxins into rivers. The dyeing process uses more than half of the water used in the textile industry, which is known to utilize a lot of water. It is predicted that 1.3 million tons of dyes will be used at an estimated cost of \$23 billion worldwide (Kamati et al. 2024). An essential component of the human world is color. There are three types of dye: the nonionic, the cationic, and the anionic (Tehrani-Bagha et al. 2013). Each of the three dissolves in water, and even small amounts of each can be harmful.

The most prevalent dyes are synthetic ones which are formed and come in a range of hues. Colorants can be classified as either natural or synthetic. The several types of synthetic dyes, i.e., reactive, basic, dispersion, direct, and vat are categorized based on their particular uses. In addition, they are categorized according to their chemical structure and several functional groups, including triaryl-methane, azo, anthraquinone, sulfur, and phthalocyanine (Tsoutsas et al. 2023). Azo dyes constitute more than half of all textile dyes used in the textile industry (Kamati et al. 2024). The cost-effective azo dye Reactive Black 5 (RB5) is used extensively in a variety of industries, such as the paper industry, textile, plastics, leather, carpets, cosmetics, ink, shoes, polish, electroplating, colors, and mineral processing (Jalali Sarvestani and Doroudi 2020). As seen in Fig. 1, RB5's complicated chemical structure (Molecular weight: 991.82 g/mol; $C_{26}H_{21}N_5Na_4O_{19}S_6$) influences how well it degrades in the wastewater dyeing industry (Tsoutsas et al. 2023; Kamati et al. 2024).

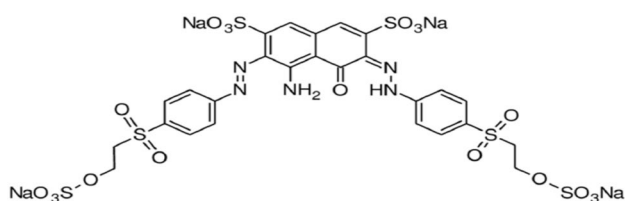


Fig. 1 Structure formula of Reactive Black 5 (RB5) ($C_{26}H_{21}N_5Na_4O_{19}S_6$)

During the coloring process, a substantial quantity of synthetic dye is disposed into the waste stream, leading to water pollution. Unprocessed dyes affect the chemical and the biological processes by reducing the light penetration, thereby disrupting photosynthesis in the aquatic environments (Reddy et al. 2012). Reactive Black 5 really has really the potential to cause environmental and health hazards when it is discharged into the environment, including water discoloration, harm to the aquatic life, and allergic reactions in humans (Kamati et al. 2024). This emphasizes the significance of eliminating RB5 from wastewater. Therefore, in order to comply to environmental requirements, before being released, the effluent needs to be treated (Amin et al. 2015). In recent years, numerous technologies have been invented to treat liquid wastes before being discharged in order to adhere to environmental standards and minimize contamination.

Dye removal from wastewater has been accomplished using a variety of methods, including physical, biological, chemical methods, or a combination of these such as ozonation (Gamoudi and Srasra 2019), coagulation (Chakraborty et al. 2022), electrocoagulation (Antonelli et al. 2024), adsorption (Gupta 2009), and membrane separation (Kumar et al. 2023). Nevertheless, it has been discovered that certain physical and chemical techniques are inadequate for totally deactivating dyes, which may result in secondary contamination when released into the environment. As a result, these methods are costly, complicated, time-consuming, and unsuccessful for large-scale dye removal, which results in the generation of sludge at the end of the process. However, adsorption is a widely used method for eliminating organic pigments from wastewater. Adsorption's cost-efficiency and sludge-free, clean operation give it an edge over competing techniques (Amin et al. 2015). Actually, one of the most effective and affordable methods for eliminating dyes from wastewater is adsorption (Gamoudi and Srasra 2019). Its inexpensive nature (Chakraborty et al. 2022), low energy consumption (Antonelli et al. 2024) and no sludge production during the cleaning process (Gupta 2009) making it the real technique for reactive dyes elimination.

Many adsorbents, including activated carbon, were employed in the adsorption process (Kumar et al. 2023), iron containing zeolites (Han et al. 2024), chitosan (Bhatt et al. 2023), and folic acid are common adsorbents for reactive dyes treatment. The Commercial adsorbents, such as the commercially available activated carbon, are very efficient but costly. Therefore, adsorbents that remove colors from wastewater at a low cost are the focus of current research (Amin et al. 2015). An adsorbent can be regarded as inexpensive if it is abundant in nature, requires little processing, or is a waste product or byproduct of another industry. Consequently, the adsorption of different pollutants from

an aqueous media has drawn a lot of attention to natural adsorbents (Jalali Sarvestani and Doroudi 2020). In recent years, one area of investigation in the adsorption dye field is the adsorption of RB5 on an adsorbent material. In fact, the easy preparation, the larger specific surface area and increased porosity structures are the advantageous factor that distinguish these materials from the others. Even with all of humanity's technological progress, going back to the earth and making use of its natural resources is still necessary. Among these, clays in all their forms (montmorillonite, illite, and kaolin) are the most important and easily accessible. Clays are chosen as adsorbents due to their cost-effectiveness, versatility, and eco-friendliness, making them ideal for the treatment of textile waste. They offer a sustainable and economical solution for pollutant removal in textile waste treatment processes (Worasith and Goodman 2023). On the other hand, the modification of clays with organo molecules can increase their adsorbent capacity. researchers have taken advantage of the chance to profit from these compounds due to their demonstrated significance (Kausar et al. 2018), ion exchange method (Korak et al. 2023), grafting (Ahmad et al. 2023) and intercalation (Thue et al. 2024) are the most methods for hybrid materials synthesis, intercalation method have emerged as a promising approach for composite synthesis due to simplest green preparation, low cost and versatility in organic molecule choice (Gürses and Güneş 2024).

Our study centers on the application of local clay; Montmorillonite (Mnt A), which we have selected to contrast with German clay; Montmorillonite (Mnt G) with their modified forms with HDTMA for Reactive Black 5 (RB5) adsorption. The materials were characterized with different analysis to identify each clays type and to confirm the successful of synthesis process, while isotherms models and pseudo-order kinetic were carried out to understood the adsorption phenomena.

Materials and methods

Raw materials

Two montmorillonite clays were used in this study. The commercial German montmorillonite (Mnt G; ~95% montmorillonite) was purchased from a German supplier, whereas the Algerian montmorillonite (Mnt A; 72% montmorillonite) was collected from the Khenchela region in northeastern Algeria. Reactive Black 5 (RB5), contains a molecular weight of 991.82 g/mol and is obtained from Sigma-Aldrich, a maximum absorbance wavelength ($\lambda_{\max}$) of 598 nm, and a chemical formula of $C_{26}H_{21}N_5Na_4O_{19}S_6$. The dye is classified as an azo-anionic compound with a

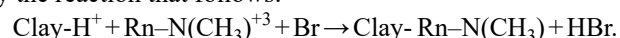
purity of 75–80%. Hexadecyltrimethylammonium bromide (HDTMAB), hydrochloric acid, and sodium hydroxide were also bought from Sigma-Aldrich (USA). All chemicals were used without further purification, and the solutions were made with deionized water.

Preparation of raw and organoclay

The raw Mnt samples were initially dried at 80 °C for 24 h, milled, and sieved. To remove soluble impurities, 50 g of raw clay was mixed with 3 L of distilled water and stirred for 24 h at room temperature (25 °C). The mixture was then transferred to a three-liter graduated cylinder and allowed to settle for 48 h. The water-washed Mnt was assembled by centrifugation (10 min -5000 rpm) to eliminate undesired fractions from the upper third of the suspension. The water-washed Mnt was subsequently dried at 80 °C for 24 h to remove residual water molecules, crushed, and stored for further use, as presented in the Fig. 2A.

2.2.1 Synthesis of modified adsorbent (Organoclay)

The organoclay was prepared by modifying the water-washed Mnt with hexadecyltrimethylammonium bromide (HDTMA). The ionization process was completed by stirring a solution comprising 10 mL of 1N hydrochloric acid and a stoichiometric quantity of HDTMA (equal to the clay's cation exchange capacity, 1 CEC) for 3 h, as indicated by the reaction that follows:



Once the HDTMA was fully ionized and dissolved, 10 g of the water-washed Mnt and left for 6 h to complete the cation exchange process. The solid phase was separated by centrifuging the resultant suspension for 15 min at 8000 rpm. The samples were washed multiple times with distilled water until bromide ions were completely removed, confirmed via a silver nitrate test. The final product was dried at 70 °C for 24 h, finely ground in a mortar, as seen in the Fig. 2B, and labeled as Mnt AM and Mnt GM.

Methods of analysis and characterization

With a Bruker D8 Advance Diffractometer, X-ray diffraction (XRD) was used to examine the mineralogical characteristics of both raw and modified Mnt. Using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 40 mA, the measurements were performed with a total analysis time of 20 min. The scanning was done over a 2θ range of 0°–80° at a step size of 4°/min.

Fourier-transform infrared spectroscopy (FTIR) was employed to investigate the surface functionalities of natural and modified Mnt. Spectra were recorded using

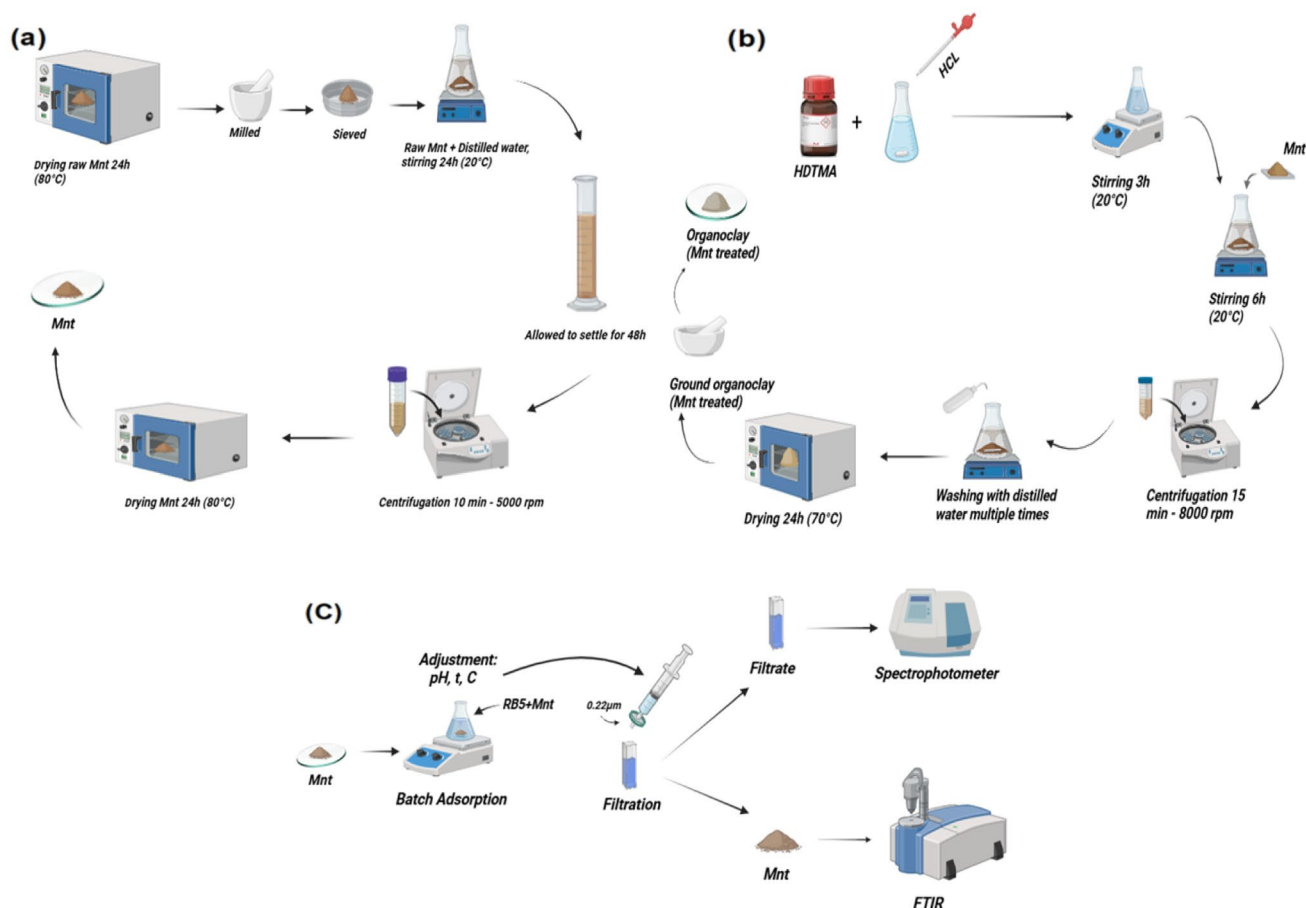


Fig. 2 (A) Processing steps for water-washed Mnt; (B) Chemical activation of Mnt using HDTMA and HCL; (C) Experimental process for the adsorption of RB5 using Mnt as adsorbent

a PerkinElmer 783 spectrophotometer over the range of $4000\text{--}400\text{ cm}^{-1}$, utilizing the KBr pellet technique with 32 scans per sample.

The chemical composition of the samples was determined via X-ray fluorescence (XRF; ZETIUM model). Sample preparation involved grinding 20 g of the material to a particle size of $90\text{ }\mu\text{m}$ within 4 min using a HERZOG grinder, aided by two drops of triethanolamine (TEA). Pellets were prepared by pressing 8 g of the ground sample at 150 kN for 10 s using a HERZOG press.

Particle size distribution (PSD) was assessed using a Microtrac S3500 laser granulometer. Powdered samples were scattered in distilled water and sonicated prior to analysis. Using dynamic light scattering (DLS), synthetic Mnt was further examined. Using a Zeta Sizer Nano ZS (Malvern) at room temperature, zeta potential (PZ) measurements were performed on Mnt suspensions in distilled water, with results referred to $25\pm 2\text{ }^{\circ}\text{C}$.

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were used to examine thermal stability and decomposition behavior using an SDT Q600 V20.9

instrument in a nitrogen environment at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$.

To investigate the connection between the pH of the solution and the adsorbent surface charge, the point of zero charge (pH_{pzc}) was established. Using a 0.01 M NaCl solution and a pH range of 1–12, HCl and NaOH were added. In each test, 50 mL of NaCl at a specific pH was mixed with 0.15 g of adsorbent and stirred at 350 rpm for 24 h. Final pH values were measured using a pH meter (Hamdi and Srasra 2014).

The cation exchange capacity (CEC) was evaluated using the copper ethylenediamine complex ($(\text{EDA})_2\text{CuCl}_2$). The amount of $\text{Cu}(\text{EDA})_2^{2+}$ adsorbed was determined by measuring the concentration difference between the initial solution and the supernatant after adsorption and centrifugation (Hamdi and Srasra 2014).

Visible absorption spectra of solution samples were analyzed using an Agilent Cary 7000 dual-beam spectrophotometer, coupled with Cary Win UV Scan data acquisition software. Quartz cuvettes with a 1 cm optical path length were used for all analyses.

Batch mode experimentation

The impact of several factors on the adsorption capacity of natural and modified Mnt for the RB5 dye was assessed by batch adsorption studies. In each experiment, 0.05 g of adsorbent was added to 50 mL conical vials containing 50 mL of a synthetic RB5 dye solution with varying initial concentrations stretching from 25 to 300 mg/L. Under carefully monitored conditions, the vials were put in a shaking incubator with a stirring speed of 100 rpm and a continual contact time of 60 min, and an ambient temperature of 25 °C. The effects of pH, contact time, and dye concentration were examined while maintaining the same level of control over all other experimental parameters. At specified time intervals, a 2 mL aliquot was withdrawn from the solution, and the Mnt was separated using a microfilter. According to Fig. 2C, a T80+UV/Vis spectrophotometer was used to measure the amount of residual RB5 in the filtrate at a wavelength of 598 nm. The amount of RB5 adsorbed per gram of adsorbent was quantified using a standard equation that included the adsorption capacity of the adsorbent (q_e ,

mg/g) and the amount of RB5 adsorbed at time t (q_t , mg/g). These equations are as follows:

$$q_e = ((C_0 - C_e)/m)V \quad (1)$$

$$q_t = ((C_0 - C_t)/m)V \quad (2)$$

where the concentrations of RB5 ions at initial, t time, and equilibrium are denoted by C_0 , C_e , and C_t (mg/L), respectively. V is the dye solution's volume (L), and m is the adsorbent's mass (g).

Theoretical basis for kinetic and isotherm adsorption modeling

Various theoretical models have been employed in the literature to describe adsorption kinetics and isotherms. In the current study, two models first-order and second-order were used to examine the kinetics of RB5 adsorption. Additionally, three isotherm models were applied to evaluate adsorption behavior: Langmuir, Freundlich and Temkin. Table 1 presents the original and linearized equations for these models, along with the corresponding plots used for data analysis.

Table 1 Equations and relevant parameters of the models for the kinetic and isotherm studies

Model	Equation	Relevant parameters
PFO	$q_t = q_e (1 - e^{-K_1 t})$	q_e and q_t (in mg/g) are the adsorbed amount of dye at the end and at time t , respectively K_1 (1/min) and K_2 (g/mg·min): constants of PFO and PSO models
PSO	$q_t = \frac{q_e^2 \cdot k_2 \cdot t}{1 + q_e \cdot k_2 \cdot t}$	
Langmuir	$q_e = \frac{Q_{\max}^0 \cdot k_L \cdot C_e}{1 + k_L \cdot C_e}$	q_e (in mg/g) is the adsorbed quantity of RB5 dye at equilibrium C_e (mg/L): concentration of adsorbate at equilibrium $Q_{\max}^0$ (mg/g): maximum monolayer adsorption capacity of Langmuir K_1 (L/mg): Langmuir constant K_F [(mg/g) (L/mg) ^{1/n_F}]: Freundlich constant n_F : dimensionless Freundlich intensity parameter
Freundlich	$q_e = K_F \cdot C_e^{1/n_F}$	
Temkin	$q_e = B \cdot \ln(A \cdot C_e)/B = (R \cdot T)/b$	A (L/mg) Temkin binding constant B (mg/g) Temkin constant b (J/mol) Temkin heat-related constant R (J/mol·K) Universal gas constant=8.314 T (K) Absolute temperature

Results and discussion

Characterization of raw clays and modified clays (Organoclay)

Grain size analysis

Granulometric analysis, illustrated in Fig. 3 and summarized in Table 2, highlights the particle size distribution of the studied clays. German clay (Mnt G) is predominantly silt-rich, comprising 3.48% clay, 94.42% silt, and 2.1% sand. Similarly, Algerian clay (Mnt A) is primarily silt-rich but contains a higher proportion of clay 11.68%, along with 83.15% silt and 5.17% sand. Following modification, both clay types exhibit a reduction in the fine particle fraction (<2 µm). For example, the clay content in Mnt G decreases from 3.48 to 2.1%, while in Algerian clay (Mnt A), it decreases from 11.68 to 3.55%. This reduction is attributed to the dispersion of clay particles during surfactant modification. As clay particles agglomerate with larger particles (silt and sand), their relative proportion in the fine fraction diminishes. This phenomenon, known as particle redistribution, is a well-documented effect of clay modification processes (Barhoumi et al. 2019, 2021).

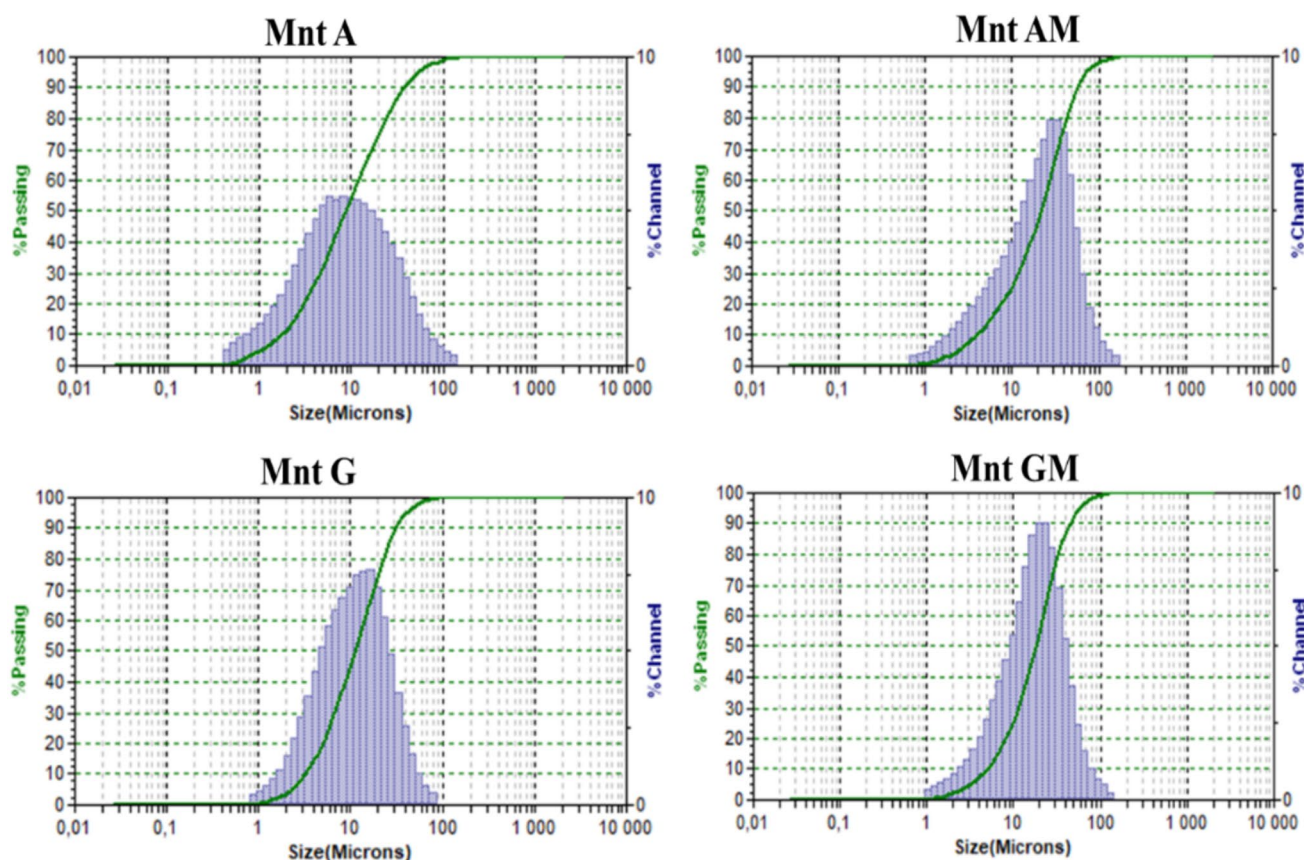


Fig. 3 Dispersion of particle size and cumulative weight percentage (green curves) of the studied clays

Table 2 The grain size analysis results

	Sand (2 mm–63 μ m) (%)	Silt (63 μ m–2 μ m) (%)	Clay (<2 μ m) (%)
Mnt A	5.17	83.15	11.68
Mnt AM	12.29	84.16	3.55
Mnt G	2.1	94.42	3.48
Mnt GM	6.44	91.46	2.1

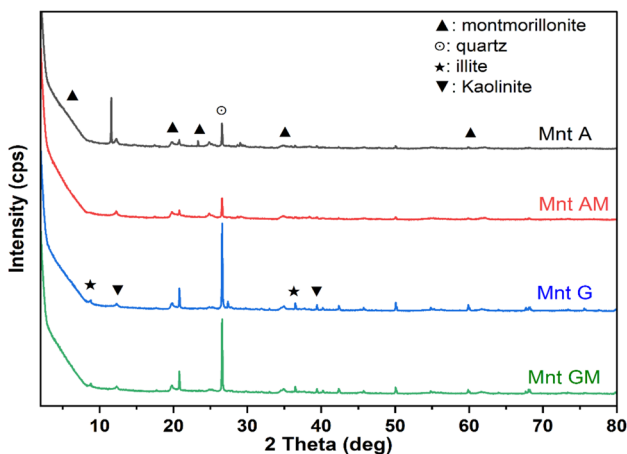


Fig. 4 The XRD patterns of different samples

Mineralogy

X-ray diffraction (XRD) analysis was used to determine the natural clays' mineralogical composition in various samples. Characteristic peaks of montmorillonite were predominantly observed at 5.17°, 19.63°, 35°, and 60° in both Mnt A and Mnt G clays are shown in Fig. 4 (Mekidiche et al. 2021). With quartz identified as the primary impurity at 26.7°. Additionally, minor impurities such as illite and kaolinite were detected in Mnt G clay, with peaks at 8.60° and 36.49° for illite, and at 12.26° and 39.3° for kaolinite. These findings align with commonly reported mineralogical compositions of natural clays (Antosik et al. 2023; Feng et al. 2017). It is important to note that the intensity of XRD peaks depends on the material being analyzed and its crystallinity, emphasizing the need for proper calibration (Antosik et al. 2023). Furthermore, the modification of Mnt clays with hexadecyltrimethylammonium bromide (HDTMA) did not affect their crystalline structure, as the position of the basal peak d_{001} (5.17°) remained unchanged. This lack of effect may be attributed to the adsorption of HDTMA on the external surfaces of the various clays without intercalation into interlayer space.

The FTIR spectrum as presented in Fig. 5, the RB5 spectrum reveals several key functional groups essential to its structure and properties. The broad band seen between 3300 and 3500 cm^{-1} suggests the presence of primary amine functionalities, which are equivalent to stretching vibrations of -NH . The presence of aliphatic chains in the dye structure is further supported by the distinctive peaks at 2888–2968 cm^{-1} , which are related to the stretching vibrations of aliphatic C-H bonds. The range of peaks between 1626–1748 cm^{-1} includes C=C stretching vibrations, characteristic of aromatic compounds, whereas carbonyl stretching vibrations are responsible for the noticeable peak at 1740 cm^{-1} , suggesting the presence of additional functional groups capable of interacting with other substances. Furthermore, the dye's distinctive characteristic, the stretching

vibrations of the azo (-N=N-) bond, are represented by the band at 1495 cm^{-1} . Lastly, the noticeable signal at 1145 cm^{-1} shows that sulfonic acid ($\text{-SO}_3\text{H}$) groups are present, which greatly improve RB5's solubility and reactivity in aqueous solutions (Ben Mbarek et al. 2017, 2023; Vinayak and Singh 2022).

Regarding HDTMA spectrum as seen in Fig. 5 shows a broad band observed in the range of 3000–3500 cm^{-1} is associated with the stretching vibrations of the amine (-NH) groups, confirming the presence of the quaternary ammonium structure in HDTMA. While, the series of peaks between 2850 and 2920 cm^{-1} and the peaks around 1375 cm^{-1} and 1450 cm^{-1} corresponding to the stretching vibrations of the aliphatic CH_2 groups, indicating the long hydrocarbon chain (Ciurac et al. 2017). The distinctive

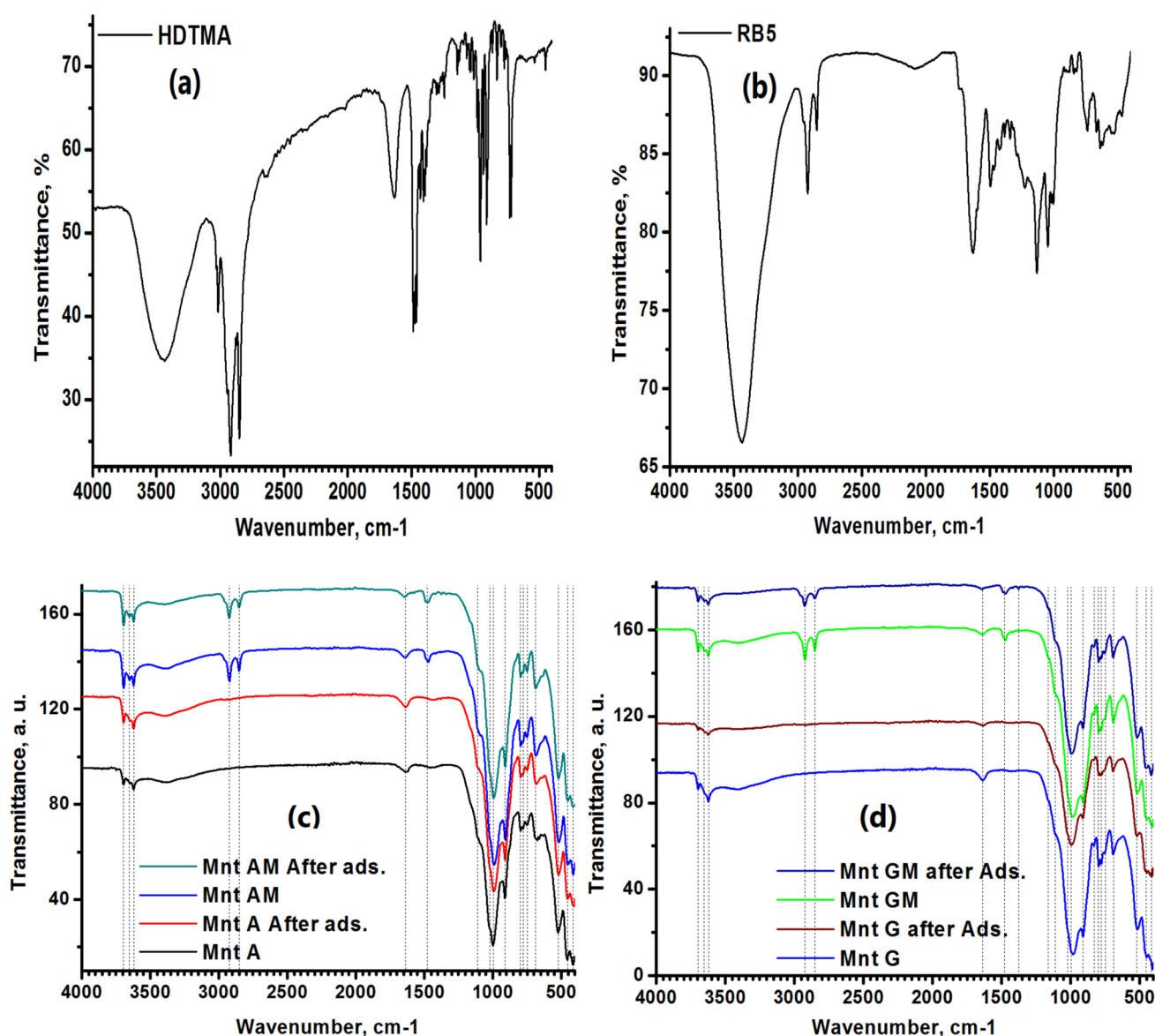


Fig. 5 The FTIR spectrum Analysis of HDTMA (a), RB5 (b), Natural and HDTMA- or/and RB5 Modified Clays (c, d)

peaks around 1000–1100 cm^{-1} , which correspond to the C–N stretching vibrations, validate the existence of amines and quaternary ammonium compounds. Additionally, the presence of the bromide ion in the HDTMA structure is shown by the peak about 620–650 cm^{-1} that corresponds to C–Br stretching vibrations (Zulu et al. 2020; Aroke and El-Nafaty 2014).

Furthermore, the FTIR analysis was conducted to ascertain the presence of HDTMA in various natural clays. The FTIR spectra as shown in Fig. 5 revealed characteristic stretching vibrations of kaolinite and illite hydroxyl groups (OH) at approximately 3699 and 3652 cm^{-1} (Shi et al. 2015; Dinh et al. 2022) which is improved by XRD results, whereas the presence of inner OH groups can be seen around 3624 cm^{-1} . Furthermore, Si–O–Si and Si–O–Al bending vibrations were identified as the source of the bands at 462 cm^{-1} and 531 cm^{-1} , respectively, while bands at 912 cm^{-1} and 795 cm^{-1} corresponded to Al–Al–OH and Al–Fe–OH bending vibrations of natural clays (Dutta and Singh 2015). The Si–O–Si stretching vibration was identified as the source of the band at 1031 cm^{-1} (Antosik et al. 2023; Shi et al. 2015).

All changed clay spectra showed new bands at 2936 and 2871 cm^{-1} after clays were transformed with HDTMA. These bands were ascribed to the CH_2 and CH_3 groups of HDTMA molecules (Dinh et al. 2022; Biglari et al. 2018). These results confirm the successful modification of the clays with HDTMA.

As shown in Fig. 5c and d, the FTIR spectra of both natural and HDTMA-modified montmorillonite before and after RB5 adsorption revealed noticeable spectral changes, indicating interactions between the dye molecules and the clay surfaces. A slight appearance of new peaks was observed in the 1300–1350 cm^{-1} region after adsorption for both natural and modified clays; however, this effect was more pronounced in the modified samples. This band is attributed to aromatic C–N stretching or a shifted sulfonate ($-\text{SO}_3^-$) vibration, originally located at 1145 cm^{-1} in free RB5, suggesting coordination with surface cations or formation of inner-sphere complexes.

A slight decrease in the intensity of the aliphatic C–H stretching bands at 2888–2968 cm^{-1} was also observed after RB5 adsorption onto HDTMA-modified clays, which may indicate direct interaction between the dye molecules and the surfactant chains. Additionally, the broad O–H stretching band in the 3100–3500 cm^{-1} region became noticeably flattened, suggesting hydrogen bonding between surface

hydroxyl groups and dye functional groups (e.g., $-\text{NH}_2$ or $-\text{SO}_3^-$) or displacement of adsorbed water by dye molecules.

Moreover, slight decreases in the intensity of the bands at $\sim 1640 \text{ cm}^{-1}$ and 3620–3700 cm^{-1} were detected post-adsorption. The reduction at $\sim 1640 \text{ cm}^{-1}$ is associated with decreased interlayer or adsorbed water, whereas the reduction at 3620–3700 cm^{-1} indicates interactions between surface hydroxyl groups and dye molecules.

Finally, the disappearance of the RB5 characteristic azo band at 1495 cm^{-1} ($-\text{N}=\text{N}-$ stretching) suggests involvement of the azo group in adsorption possibly through $\pi-\pi$ stacking or electrostatic interactions or partial degradation of the dye structure.

Chemical composition

X-ray fluorescence (XRF) analysis was conducted to determine the chemical composition of montmorillonite clay samples from Algeria (Mnt A) and Germany (Mnt G). As shown in Table 3, both clay types exhibit high silica content, primarily due to the presence of clay minerals and quartz. Mnt A and Mnt G contain 48.10% and 32.41% clay minerals, respectively. Additionally, significant aluminium content was observed, with 15.95% in Mnt A and 11.60% in Mnt G, confirming the aluminosilicate nature of the clays, which is characteristic of the smectite group (Barhoumi et al. 2019). The calculated $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios for Mnt A and Mnt G are 0.33 and 0.35, respectively. These values closely match the expected ratio (0.33) for montmorillonite (Mekidiche et al. 2021), further corroborating the identification of this clay mineral. The reddish and brownish coloration of the clay samples is attributed to the presence of Fe_2O_3 . The Algerian sample (Mnt A) exhibits a higher Fe_2O_3 concentration (8.02%) compared to the German sample (Mnt G), which contains 5.30%. Both samples also display moderate amounts of CaO, likely associated with smectite and carbonate minerals such as calcite. The low Na_2O content suggests a predominance of calcium-rich clay minerals (Nweke et al. 2015). In addition, minor quantities of other metal oxides, including K_2O , MgO were detected in both samples (Oloyede et al. 2021).

Zeta potential

One important measure for evaluating the stability of clay dispersions is the zeta potential. Hexadecyltrimethylammonium bromide (HDTMA) was used to modify the Algerian (Mnt A) and German (Mnt G) montmorillonite clays, as

Table 3 Chemical compositions of Algerian and German natural clays (%)

Element (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	IL
Mnt A	48.10	15.95	8.02	7.19	4.78	1.62	1.61	13.07
Mnt G	37.41	11.60	5.30	23.36	0.85	1.01	1.54	19.13

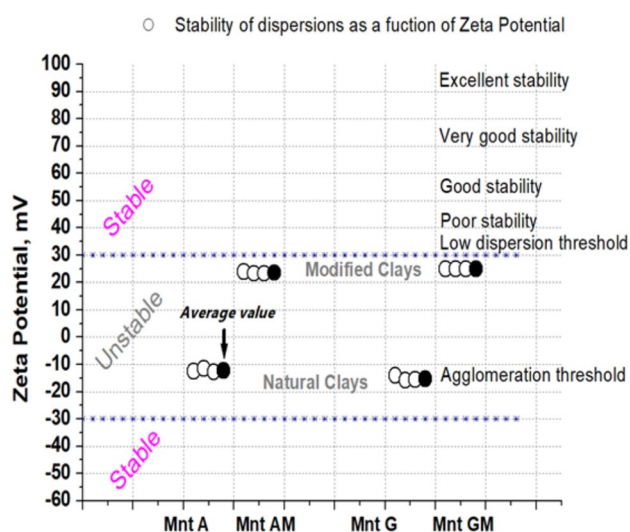


Fig. 6 Zeta potential of natural and modified clay

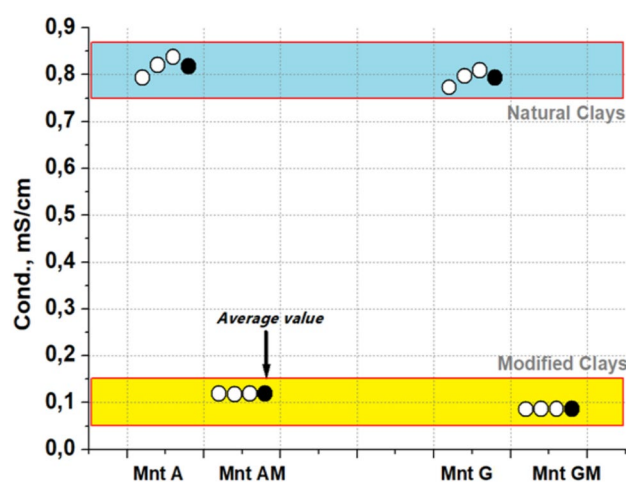


Fig. 7 Electrical conductivity of natural and modified clay

shown in Fig. 6. This resulted in a significant rise in their zeta potential values, reaching about +29 mV, indicating successful surface functionalization. Surface modification with cationic surfactants significantly alters the physico-chemical properties of montmorillonite, particularly its zeta potential. The surface of the modified clay changed to positive values, but the zeta potential of raw montmorillonite was negative. By encouraging stronger electrostatic interactions with anionic dyes, this modification increases the modified clay's adsorption capacity (Mahmoodi et al. 2019). especially Reactive Black 5 (RB5), the target dye under investigation in this work.

Naturally, Mnt A and Mnt G both have negative zeta potential values between -10 and -20 mV. This is because they have naturally occurring mineral components including calcite and quartz as well as negatively charged surface functional groups. The HDTMA modification method

effectively reverses the surface charge, resulting in a positive zeta potential of +20 to +30 mV (Hojiyev et al. 2016). Clay suspensions with zeta potential more than +30 mV or less than -30 mV value are typically regarded as stable, according to Tunç et al. (2012).

Electrical conductivity

For assessing the electrical conductance of materials, such as colloids and clay-rich porous materials, electrical conductivity is an essential metric (Hasan et al. 2018).

The study's findings, which are shown in Fig. 7, showed that the modified clays had reduced electrical conductivity values between 0.0860 and 0.119 mS/cm, whereas the natural clays had values between 0.793 and 0.818 mS/cm. This decline is explained by the substitution of bigger, less mobile organic HDTMA⁺ ions for tiny, highly mobile inorganic cations like Na⁺ and Ca²⁺. This lowers electrical conductivity by reducing the number of charge carriers. These results align with earlier research (He et al. 2006), which stated that because organic alteration blocks active sites and reduces porosity, conductivity is decreased.

Additionally, the effective intercalation and ion exchange of HDTMA molecules into the interlayer gaps were restricted by the relatively low temperature (25 °C) at which the modification was performed.

Furthermore, the clay utilized in this investigation was cleaned with water alone no acid purification or other pre-treatment was applied so it maintained some naturally occurring contaminants before alteration. may still be present, which could have an impact on the surface structure and conductivity behavior (e.g., quartz, feldspar, iron oxides).

Moreover, conductivity may be impacted by variables like surfactant loading and solution pH. While pH changes can have an impact on surface charge distribution and inter-layer ion behavior, high surfactant loading can produce dense organic layers that restrict ion mobility.

The modified clay's adsorption capacity was also greatly increased by the surface charge (zeta potential) shifting to positive values following alteration. This improved electrostatic interactions with anionic pollutants like Reactive Black 5 (RB5).

The modified clay's adsorption capacity for RB5 was significantly higher than that of the raw clay, despite the observed decrease in conductivity. This was explained by the improved surface charge.

Electrophoretic mobility

One important factor affecting the surface charge distribution and electrokinetic behavior of clay particles is their

electrophoretic mobility (EM) (Leroy et al. 2015; Zeng and Kobayashi 2025).

Both the original and modified clays' electrophoretic mobility profiles are shown in Fig. 8, which also shows the notable surface charge inversion brought about by the modification process. The natural clays in this investigation have negatively charged surfaces, according to the electrophoretic mobility assays, which showed values of -0.9625 and $-1.189 \mu\text{m cm/V s}$ for Mnt A and Mnt G, respectively. The presence of deprotonated hydroxyl and silanol groups at neutral pH is responsible for this negative charge.

When cationic functional groups were successfully added to improve electrostatic attraction toward anionic dyes, a significant reversal in surface charge was seen, reaching $+1.840$ and $+2.233 \mu\text{m cm/V s}$ for Mnt AM and Mnt GM, respectively. The pH of the solution was also found to have a significant impact on surface charge; lower pH values result in increased surface protonation, which amplifies the positive charge and enhances adsorption capacity.

Modified (Mnt AM) acquired a better maximum adsorption capacity (Q_{max}) for Reactive Black 5, despite modified (Mnt GM) exhibiting higher electrophoretic mobility, according to adsorption studies. This suggests that additional variables, including effective surface area, pore size distribution, and particular physicochemical interactions between the adsorbent and the dye molecules, also impact adsorption effectiveness in addition to surface charge. When assessing adsorbent performance, this distinction highlights the significance of taking into account a variety of factors.

TGA/DTG

The modification of clays (Mnt A) and (Mnt G) with HDTMA was reconfirmed through TGA analysis and derivative thermogravimetric (DTG) analysis, as illustrated in Fig. 9a, b. The thermograms of the natural clays (Mnt A)

and (Mnt G) exhibited three stages of mass loss within the temperature range of 25 – 900 °C. Initially, the first mass loss occurred between 25 and 200 °C, with DTG peaks around 75 °C and 140 °C as seen in Fig. 9c, d, indicating the evaporation of physisorbed and intercalated water molecules present within the interlayer spaces and cavities of the clay crystal structure (El-Kordy et al. 2023). The mass loss was more pronounced for Mnt A (5.77%) and Mnt G (4%) likely due to the higher adsorption capacity of montmorillonite present in Mnt A and Mnt G, as confirmed by XRD analysis.

Subsequently, no mass loss was observed between 200 and 400 °C, displaying the relative stability of the clays within this temperature range, with no discernible DTG peaks. The second stage occurred between 400 and 600 °C, with DTG intensity peaks at 500 °C for natural clay (Mnt A), likely attributed to the dihydroxylation of structural OH groups, releasing water (Mekidiche et al. 2021; Abeywardena et al. 2017). Mnt A clay exhibited the highest mass loss (5.78%), possibly due to the higher concentration of surface hydroxyl groups in Mnt A. In contrast, Mnt G exhibited lower mass loss (1.07%) with no discernible DTG peaks, suggesting a lower quantity of surface hydroxyl groups compared to the other clays.

The final stage occurred within the temperature range around 600 to 900 °C, with DTG peaks at 714 °C for natural clay (Mnt G) attributed to the degradation of carbonate and decay of the clay's structure, releasing certain mineral by products (Hazarika et al. 2024; Erdogmus et al. 2022).

Following modification with HDTMA, a new mass loss was observed between 200 and 400 °C, with DTG peaks approximately 251 and 410 °C for modified clays (Mnt AM) and (Mnt GM), attributed to the decomposition of HDTMA molecules (Dinh et al. 2022; El-Kordy et al. 2023). Additionally, the TGA curves of modified clays (Mnt AM) and (Mnt GM) exhibited a lesser initial weight loss of adsorbed water molecules compared to unmodified clays (Mnt A) and (Mnt G), confirming the successful replacement of water by HDTMA molecules. Furthermore, the highest mass loss observed for HDTMA-modified clays; Mnt AM (9.14%) and Mnt GM (8.17%) compared to other clays, attributed to the presence of montmorillonite in both clays, which has a high potential for organic molecules intercalation.

Cation exchange capacity

The cation exchange capacity (CEC) of the two montmorillonite clays under study was high, with values of 44 mequiv/100 g for Mnt G and 41.33 mequiv/100 g for Mnt A. These values are characteristic of montmorillonite, a smectitic clay mineral known for its exceptional CEC due to its unique layered structure, high surface area, and interlayer spaces capable of accommodating exchangeable

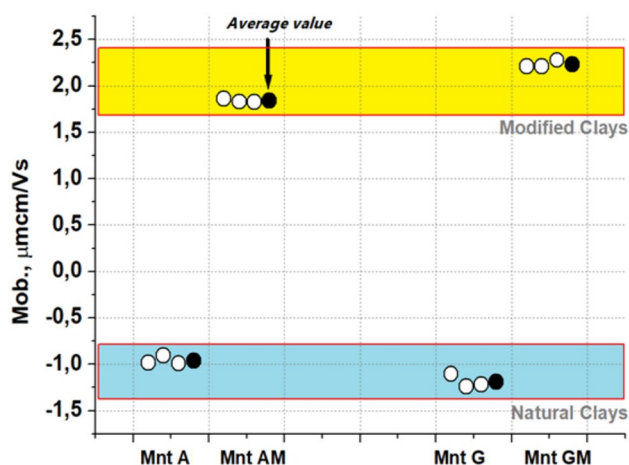


Fig. 8 Electrophoretic mobility of natural and modified clay

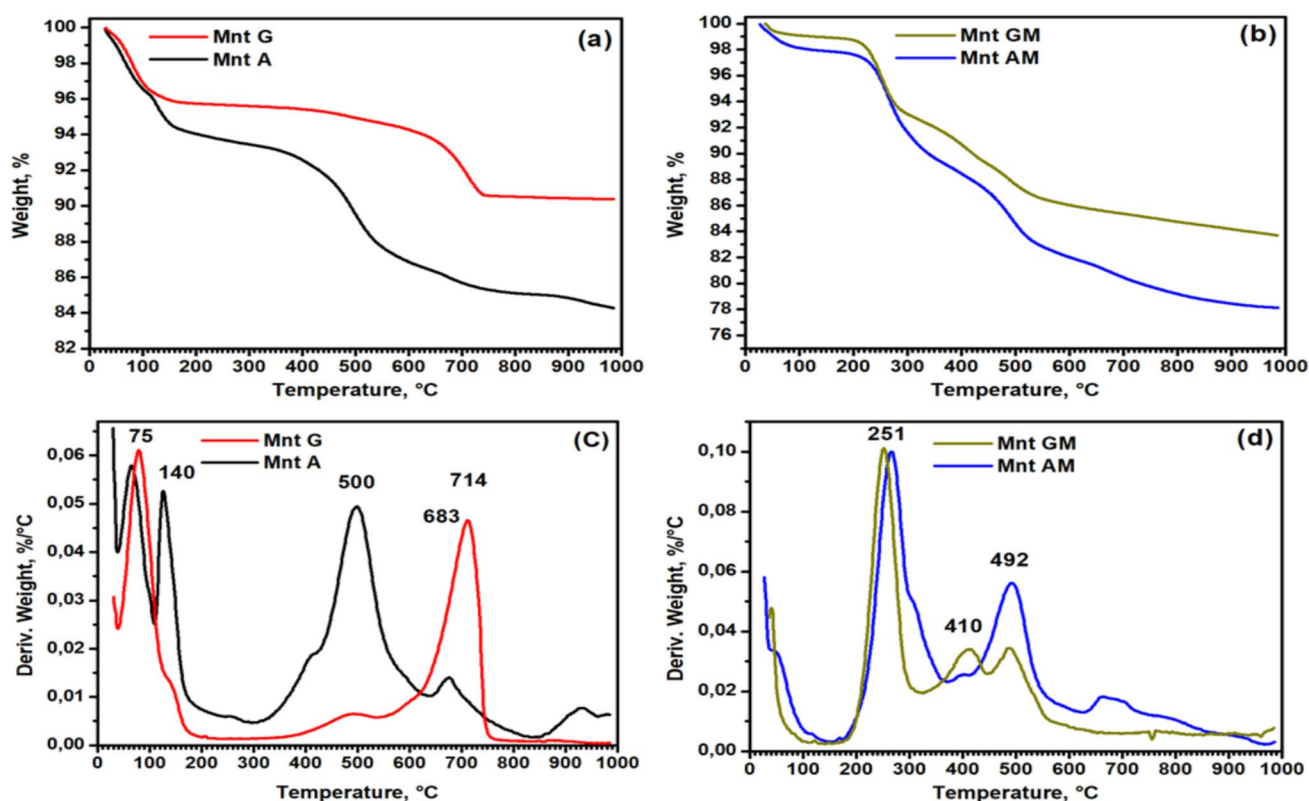


Fig. 9 TGA/DTG analysis of natural (a, c) and modified clays (b, d)

cations (Barhoumi et al. 2021). Such properties make montmorillonite highly effective in applications like adsorption, catalysis, and soil fertility enhancement.

Adsorption of RB5 dye

Impact of pH on RB5 adsorption

The pH of the solution significantly influences the adsorption of Reactive Black 5 (RB5) dye onto both modified and unmodified clay adsorbents, mostly as a result of the clay's and the dye molecules' pH-dependent surface charges. pH_{pzc} (point of zero charge) values for the clays, are shown in Fig. 10, ranged from 4.88 to 7.2, indicating that the clay surface is positively charged at solution pH values below the pH_{pzc} . This explains the higher adsorption efficiency observed in acidic conditions, since the negatively charged molecules are more successfully attracted to the positively charged clay surface. As shown in Fig. 11, maximum RB5 removal occurred at pH 2 for all clay samples. These results can be explained by the high positive surface charge of raw clay and organoclays at low $pH < pH_{pzc}$ (Munagapati et al. 2018). In fact, at low pH, the clay surface obtains a positive charge, which enhances electrostatic attraction with the anionic RB5 dye molecules. Conversely, as pH increases,

the positive surface charge diminishes, leading to weaker interactions and reduced adsorption.

Experimental results revealed that the adsorption capacity of all adsorbents increases as the pH decreases. These results are according to earlier research, demonstrate that when the pH increased, the RB5 adsorption reduced (Silva et al. 2018). For example, at a constant initial aqueous concentration of 300 mg/L the RB5 adsorption was evaluated to be equivalent to 20.22 and 25.55 mg/g by Mnt A and Mnt AM and 19.89 and 23.15 mg/g by Mnt G and Mnt GM at pH 12. These amounts increased up to 23.18 and 27.66 mg/g by Mnt A and Mnt AM and 22.08 and 26.02 mg/g by Mnt G and Mnt GM, respectively at pH of 2. This increase may be explained by the medium's pH, which makes the charge repulsive at higher pH and appealing at lower pH ($< pH_{pzc}$). This pattern can be explained by the greater electrostatic forces in acidic conditions, where the negatively charged SO_4^- groups in RB5 molecules interact more successfully with the positively charged clay surface. As a result, adsorption and electrostatic forces are stronger in acidic liquids. At low pH levels efficiency will be higher (Jalali Sarvestani and Doroudi 2020). In alkaline media, an excessive amount of OH^- ions compete with RB5 for adsorption sites, and the clay surface loses its positive charge, further weakening the electrostatic forces (Bhaumik et al. 2016). Therefore, the

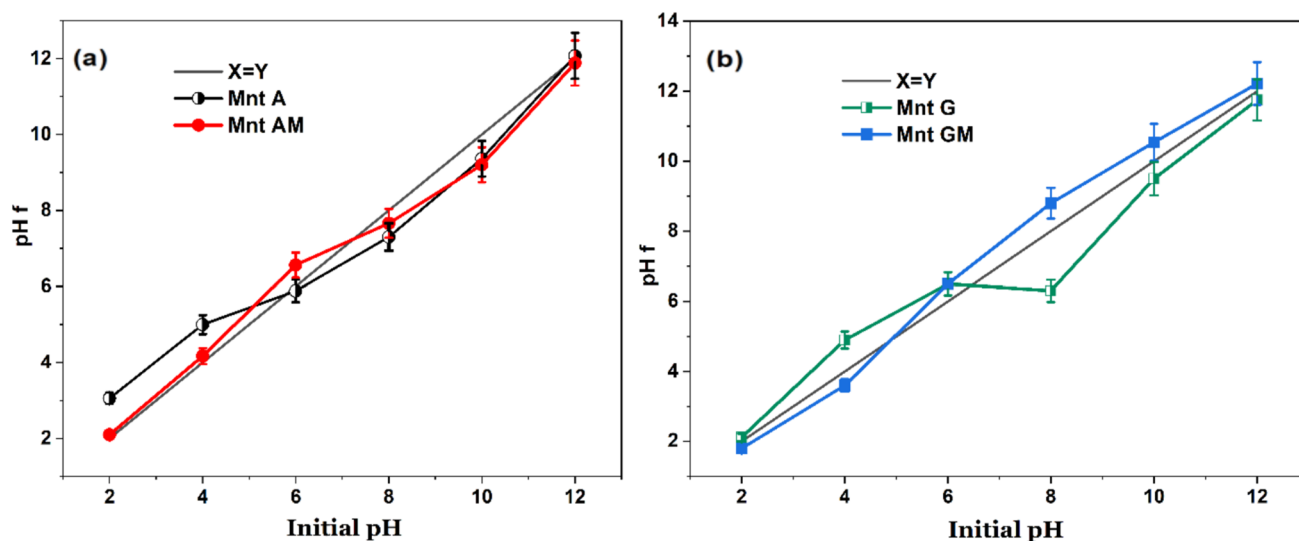


Fig. 10 pH_{pzc} of different materials

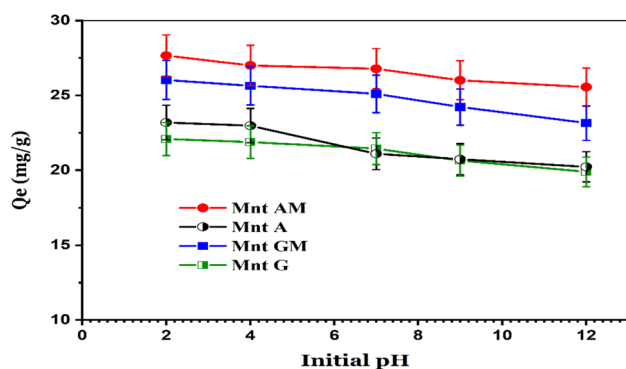


Fig. 11 Effect of initial pH on the adsorption efficiency of RB5 on clays [$m/V = 1 \text{ g/L}$, Time = 60 min, $C_0 = 100 \text{ mg/L}$]

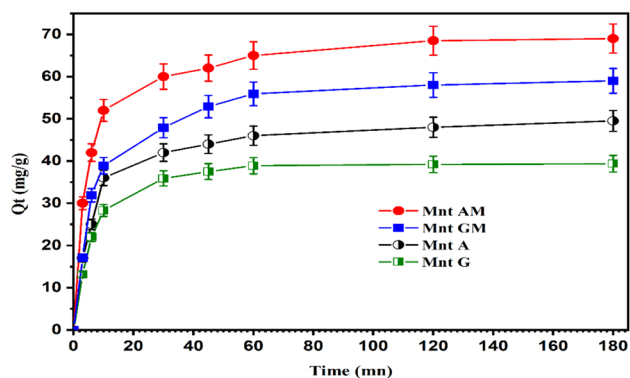


Fig. 12 Adsorption of RB5 dye by natural and modified clays [$m/V = 1 \text{ g/L}$, $C_0 = 100 \text{ mg/L}$, $pH = 2$]

removal efficiency and adsorption capacity decrease as the pH rises from 2 to 12.

Effect of contact time: kinetic study

Adsorption kinetics describe the rate at which RB5 molecules are adsorbed onto the clay surface. The effect of contact time on RB5 adsorption onto natural and modified clays is illustrated in Fig. 12. According to the results, the adsorption capacity of all clay samples approached equilibrium within 60 min of contact time. Additionally, modified clays consistently demonstrated higher efficiency compared to their natural counterparts. The adsorption capacities of the studied clay samples for RB5 dye ranged from 39.4 mg/g to 69 mg/g, following the order: Mnt AM > Mnt GM > Mnt A > Mnt G. The superior performance of modified clays can be attributed to the presence of the HDTMA surfactant, which enhances the adsorption mechanism, making them more effective at capturing dye molecules. The rapid attainment of equilibrium for the studied clays is particularly advantageous for practical applications. It reduces energy consumption during agitation, thereby improving the economic viability of the adsorption process.

The calculation of kinetic parameters enables the scaling of adsorption operations to reactors with smaller capacities. The Pseudo-First-Order (PFO) and Pseudo-Second-Order (PSO) models, two popular kinetic models seen in Fig. 13, were fitted to time-dependent experimental data (Abeywardena et al. 2017). The equations and parameters for these models are provided in Table 3. A lower chi-square (χ^2) value and a higher regression coefficient (R^2) indicate better accuracy of a model in describing the adsorption data. Table 4 summarizes the adsorbed quantities (q_1 , q_2), the

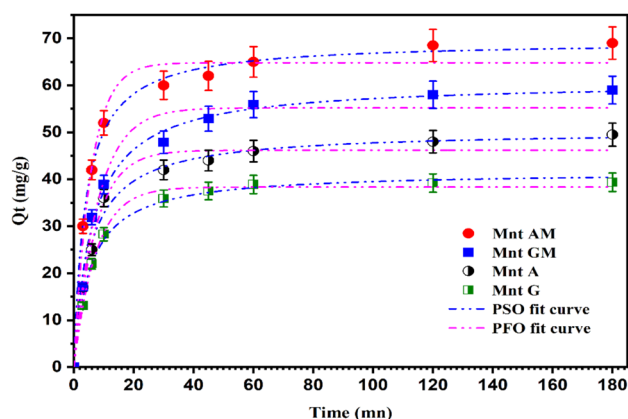


Fig. 13 Non-linear Kinetic model fitting of PFO and PSO model [$m/V = 1 \text{ g/L}$, $\text{pH} = 2$, $C_0 = 100 \text{ mg/L}$]

Table 4 Determined parameters of non-linear kinetic models for the RB5 adsorption ions onto clays

Model	Unit	Mnt A	Mnt AM	Mnt G	Mnt GM
Q_{exp}	mg/g	49.5	69	39.36	59
Pseudo first order					
q_1	mg/g	46.17138	64.80279	38.34802	55.2039
K_1	1/min	0.14046	0.17908	0.13694	0.12652
R^2	—	0.98449	0.98233	0.99595	0.97883
χ^2	—	5.0381	10.45032	0.90632	10.15359
Pseudo second order					
q_2	mg/g	50.32575	69.41992	41.63968	60.74625
K_2	g/mg.min	0.00368	0.00373	0.00445	0.00264
R^2	—	0.99299	0.99697	0.99537	0.99392
χ^2	—	2.27774	1.79097	1.03678	2.91869

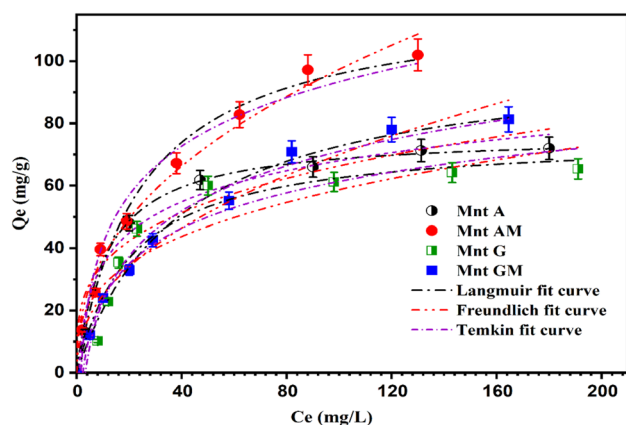


Fig. 14 Non-linear isotherm models fitting for RB5 adsorption (Langmuir, Freundlich and Temkin) [$m/V = 1 \text{ g/L}$, $\text{pH} = 2$, $C_0 = 25\text{--}300 \text{ mg/L}$, Time = 60 min]

rate constants for the PFO and PSO models (K_1 and K_2), the regression coefficients (R^2), and the chi-square (χ^2) values for the four studied adsorbents. The R^2 values for the PSO model were found to be close to unity (~ 1.0), suggesting an excellent fit, while the χ^2 values were the lowest for the PSO

Table 5 Parameters of isotherms of RB5 dye onto clays

Model	Unit	Mnt A	Mnt AM	Mnt G	Mnt GM
Langmuir					
Q_{exp}	mg/g	72	102	65.4	81.3
Q_{max}^0	mg/g	76.4	113.456	75.7	101.8
K_L	L/mg	0.088	0.055	0.047	0.025
R^2	—	0.989	0.953	0.950	0.992
χ^2	—	8.23	71.59	34.94	7.04
Freundlich					
K_F	(mg/g)·(L/mg) ^{1/n}	18.26	18.05	13.34	8.89
nF	—	3.57	2.71	3.11	2.23
R^2	—	0.93	0.975	0.854	0.980
χ^2	—	48.78	37.49	89.61	19.54
Temkin					
A	(L/mg)	1.1374	1.1838	0.4233	0.3015
B	(mg/g)	14.3631	19.6795	16.3794	20.8470
R^2	—	0.977	0.961	0.927	0.987
χ^2	—	17.94	60.19	51.20	12.22
b	J/mol	169.7	123.9	148.8	116.9

model. Furthermore, the calculated adsorbed quantity (q_2) values closely matched the experimental equilibrium data.

Based on the fitting results (R^2 and χ^2 values), when it came to fitting the experimental data, the PSO model outperformed the PFO model. This suggests that RB5 adsorption mostly takes place by chemisorption and is impacted by both RB5 concentration and adsorption site availability.

Effect of initial concentration: isotherm study

The adsorption isotherm is crucial as it describes how contaminants interact with adsorbents. The relationship between the final concentration (C_e , mg/L) and the adsorption capacity (q_e , mg/g) is determined through adsorption equilibrium experiments (Ouakouak et al. 2021). As shown in Fig. 14, the results indicate that the amount of dye removed rises with its initial concentration, ranging from 25 to 300 mg/L. It was also observed that modified clays adsorb more dye molecules compared to unmodified samples. The adsorption capacities of the studied clays for RB5 dye ranged from 65.4 mg/g to 102 mg/g, following the order: Mnt AM > Mnt GM > Mnt A > Mnt G. These findings align with the data obtained from the kinetic study, confirming the role of the HDTMA surfactant in enhancing adsorption capacity by increasing interactions between dye molecules and the clay surface.

The modeling of equilibrium data provides valuable insights into the adsorption mechanism, including affinity, binding energy, mode of adsorption, and the maximum adsorption capacity of the adsorbent. In the present study, the adsorption behavior of RB5 dye onto clay adsorbents was described using the Langmuir and Freundlich isotherm models. As indicated by the values shown in Table 5, the

Langmuir model, as opposed to the Freundlich model, which is depicted in Fig. 14, offered a superior fit to the experimental results (with the exception of Mnt AM, which was slightly better described by Freundlich; $R^2=0.975$ vs. 0.953 for Langmuir). According to the Langmuir model, adsorption occurs on a uniform surface, resulting in surface saturation at greater concentrations (Ouakouak et al. 2021). Based on the Langmuir model, the maximum monolayer adsorption capacity ($Q_{\max}$) was calculated to be 113.4 mg/g for Algerian montmorillonite modified with HDTMA (Mnt AM), followed by Mnt GM with a capacity of 101.8 mg/g. For the unmodified clays, Mnt A and Mnt G, the capacities were approximately 76.4 mg/g and 75.7 mg/g, respectively.

In addition, the Temkin isotherm model was applied to provide complementary insight into the adsorption mechanism. This model assumes that the adsorption energy decreases linearly with surface coverage due to adsorbent–adsorbate interactions. As shown in Fig. 14, all samples exhibited a reasonable fit to the Temkin model, particularly the HDTMA-modified clays. Although Mnt GM recorded the highest R^2 value (0.987) within the Temkin model, Mnt AM maintained the highest overall adsorption capacity, consistent with the Langmuir results confirming its superior performance. The Temkin model parameters (A , B , R^2 , and χ^2) are presented in Table 5. The Temkin binding constant A (L/mg) ranked the initial affinity as Mnt AM $\approx$ Mnt A $\gg$ Mnt G $>$ Mnt GM (1.1838, 1.1374, 0.4233, 0.3015). Using B (mg/g), the energy-related parameter $b=RT/B$ at 293.15 K indicated stronger average interactions on Mnt A and Mnt G (169.7 and 148.8 J/mol) than on Mnt AM and Mnt GM (123.9 and 116.9 J/mol). It is also noteworthy that the Langmuir model yielded higher R^2 values than the Temkin model for most samples, including the unmodified clays, reinforcing the conclusion that adsorption predominantly occurs on

relatively homogeneous surfaces, while the Temkin model remains a valuable complementary tool for understanding adsorption energy distribution.

Thermodynamic studies

The effect of temperature on the process of RB5 dye adsorption on the natural and modified clays was investigated at different temperatures of 25, 35, 40, 45 and 50 °C (Fig. 15). The adsorption capacity of the materials shows distinct temperature-dependent behaviors. Mnt AM consistently exhibits the highest adsorption capacity across all temperatures, suggesting strong thermal stability and superior performance. In contrast, Mnt GM shows a clear decline as temperature increases, indicating reduced efficiency at higher temperatures. Mnt A and Mnt G follow similar patterns, with a noticeable dip around 40 °C, hinting at possible thermal sensitivity or structural changes.

Thermodynamic parameters were evaluated to assess the effect of temperature on the adsorption of RB5 dye onto the used clay samples. The distribution coefficient (K_d) was determined using the following equation:

$$K_d = \frac{Q_e}{C_e}$$

where Q_e is the equilibrium adsorption capacity (mg/g) and C_e is the equilibrium concentration in solution (mg/L).

The changes in standard enthalpy (ΔH° , kJ/mol) and entropy (ΔS° , kJ/mol·K) were calculated from the Van't Hoff relation:

$$\ln \cdot K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

where R is the universal gas constant (8.314 J/mol·K) and T is the absolute temperature (K).

The Gibbs free energy change (ΔG° , kJ/mol) was obtained using Equation below:

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ$$

According to the calculated thermodynamic parameters (Table 6). The adsorption process is spontaneous at most studied temperatures, as indicated by negative ΔG° . Mnt AM and Mnt GM exhibit exothermic behavior ($\Delta H^\circ < 0$), with adsorption decreasing at higher temperatures and becoming non-spontaneous above 45–50 °C. In contrast, Mnt A and Mnt G show endothermic tendencies ($\Delta H^\circ > 0$), with spontaneity improving at higher temperatures. The positive ΔS° for Mnt A and Mnt G suggests increased randomness at the solid–liquid interface, while the negative ΔS° for Mnt AM

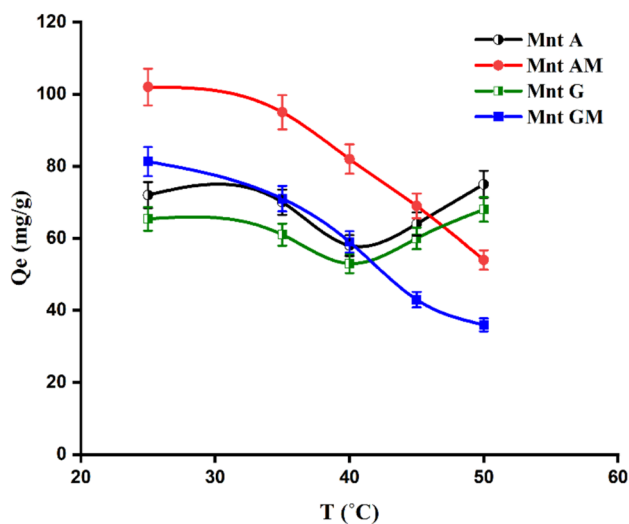


Fig. 15 Effect of temperature variation on RB5 adsorption onto natural and modified clays

Table 6 Thermodynamics parameters of RB5 dye adsorption onto natural and modified clays

Adsorbent	ΔH° (kJ/mol)	ΔS° (kJ/mol·K)	ΔG° (kJ/mol)				
			298 K	308 K	313 K	318 K	323 K
Mnt A	+9.2	+0.037	−1.96	−1.41	−0.77	−1.57	−3.43
Mnt AM	−29.0	−0.077	−3.94	−2.95	−2.07	−0.93	+0.09
Mnt G	+6.6	+0.029	−1.56	−1.25	−0.88	−1.13	−1.66
Mnt GM	−31.8	−0.078	−3.69	−2.27	−0.91	+0.67	+1.86

Table 7 The Comparison adsorption capacity for RB5 dye with various adsorbents

Adsorbent	Conditions of adsorption isotherm					$Q_{\max}$ (mg/g)	Reference
	m (g)	pH	t (min)	C_0 (mg/L)	T (°C)		
Pumpkin seed hulls	1	2	30	100	25	9.18	(Çelebi 2019)
Eggshells	0.5	6	15	100	25	18.46	(Çelebi 2019)
Banana peel biochars	0.6	3	120	75	25–65	7.58	(Kapoor et al. 2022)
CTS/MMT	10	2	60	200	60	138.89	(Umpuch and Sakaew 2015)
PAC	1	Natural	60	5–100	20	58.823	(Eren and Acar 2006)
Fly ash	10	Natural	60	5–100	20	7.936	(Eren and Acar 2006)
Activated red mud	2–10	3	60	40	25	35.58	(Shirzad-Siboni et al. 2014)
Biomass fly ash	2	8.1–8.5	1436	100	25	4.38	(Pengthamkeerati et al. 2008)
Fe ₃ O ₄ @L-arginine	0.8	3	30	50	25	89.20	(Pormazar and Dalvand 2022)
Mnt A/HDTMA	0.05	2	60	25–300	25	113.4	This study
Mnt G/HDTMA	0.05	2	60	25–300	25	101.8	This study
Mnt A	0.05	2	60	25–300	25	76.4	This study
Mnt G	0.05	2	60	25–300	25	75.7	This study

and Mnt GM reflects more ordered dye–surface interactions (Boudjemaa and Zidelkheir 2020; Amin et al. 2015; Li et al. 2018; Umpuch and Fakthaisongdechakul 2024).

Comparison with other adsorbents

The Table 7 presents a comparison of the new adsorbent materials developed in this study (Mnt AM and Mnt GM) with several other materials reported in recent literature, along with their optimal conditions for removing RB5, based on the Langmuir “ $Q_{\max}$ ” adsorption capacity. The results exhibit that for all adsorbent the best conditions for RB5 elimination are acidic. Notably, Mnt AM demonstrates a significantly higher adsorption capacity compared to other adsorbents listed in Table 7, with a maximum adsorption capacity of 113.4 mg/g. This value highlights Mnt AM as a highly effective adsorbent for RB5 elimination. In fact, its adsorption capacity is nearly three times greater than that of activated red mud (Shirzad-Siboni et al. 2014) and six times greater than that of eggshells (Çelebi 2019). Moreover, the modified clay (Mnt AM) exhibits a far superior adsorption capacity compared to other adsorbents such as powdered activated carbon (PAC), Fe₃O₄@L-arginine nanoparticles, and banana peel biochars. When compared to other modified clay minerals, Mnt AM achieves a highly competitive RB5 adsorption rate, coupled with an economical production cost. These findings suggest that Mnt AM is a promising and cost-effective material for the removal of RB5 from

aqueous solutions, making it a strong candidate for practical applications.

Proposed adsorption mechanism for Reactive Black 5 (RB5) on montmorillonite clay (Raw and modified Mnt)

A comprehensive understanding of Reactive Black (RB5) adsorption onto the raw and HDTMA-Modified Montmorillonite necessitates a thorough investigation of the underlying mechanisms as seen in Fig. 16. This adsorption phenomenon is intricately influenced by a confluence of factors, including the functional groups present within both the adsorbate and the adsorbent, the textural and surface properties of the adsorbent material, the adsorbate’s diffusional behavior towards the adsorbent surface, and the nature of the intermolecular interactions that occur between them.

The adsorption of RB5 onto raw montmorillonite likely involves a combination of interactions. Primarily driven by cation bridging Ca²⁺ or Mg²⁺, facilitates the adsorption of negatively charged RB5 molecules despite the repulsive forces from the negatively charged clay surface (Mnt (Na⁺)+RB5 (−SO₃[−]) → Na⁺-bridged complex). Hydrogen bonding between hydroxyl groups (−OH) on the clay corners and functional groups on RB5, such as sulfonic groups (−SO₃H) and amino groups (−NH₂), further enhances the adsorption (Mnt_{edge} (−OH)⋯RB5 (−SO₃[−] or −NH₂)). While weak van der Waals forces arising from interactions between

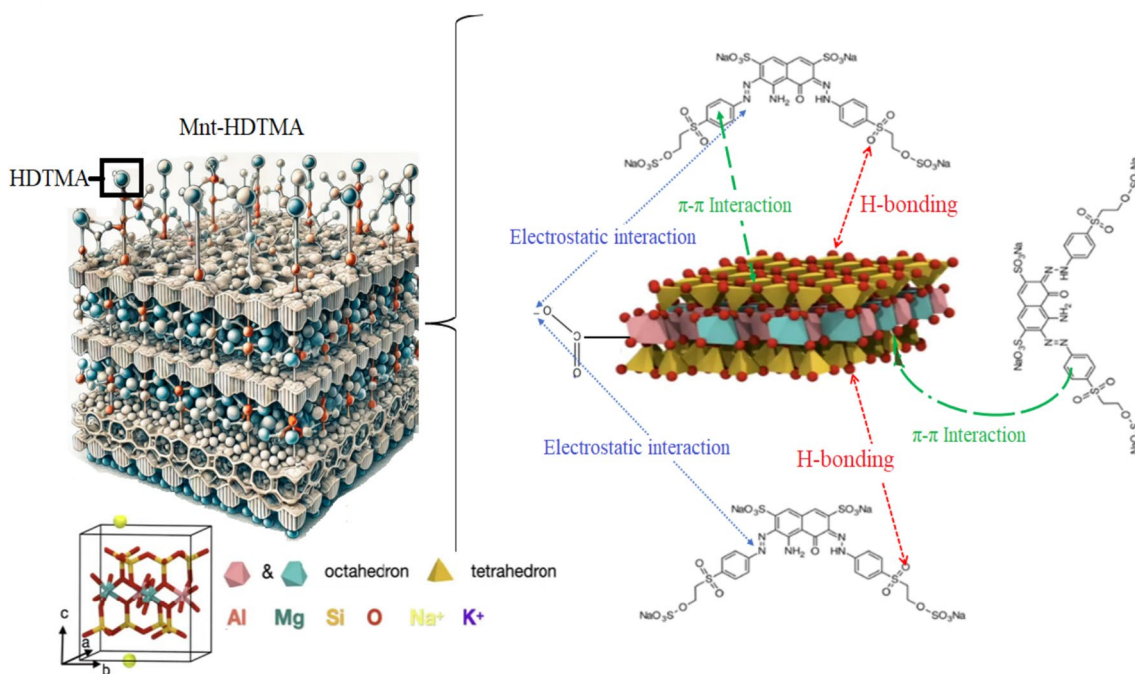


Fig. 16 Proposed Adsorption Mechanism for RB5 on Mnt

the aromatic rings of RB5 and the clay surface may also contribute to adsorption (Mnt_{surface}...RB5 aromatic structure), their overall contribution is likely minimal.

On the contrary, the adsorption of Reactive Black 5 (RB5) onto HDTMA-modified montmorillonite is significantly enhanced compared to raw montmorillonite due to several key mechanisms. Modification with hexadecyltrimethylammonium bromide (HDTMA) introduces positively charged quaternary ammonium groups ($-N^+(\text{CH}_3)_3$) to the clay surface, replacing exchangeable cations. These positively charged groups strongly attract the negatively charged sulfonic acid groups ($-\text{SO}_3^-$) of RB5, forming stable electrostatic adsorption complexes:

HDTMA-modified surface ($-N^+(\text{CH}_3)_3$) + RB5 ($-\text{SO}_3^-$) → Electrostatic adsorption complex.

In addition, the incorporation of long hydrophobic alkyl chains ($\text{C}_{16}\text{H}_{33}$) from HDTMA into the clay interlayer creates hydrophobic domains. These domains promote strong hydrophobic interactions with the nonpolar aromatic regions of RB5: (HDTMA Alkyl Chains ... RB5 Aromatic Rings). Furthermore, π - π stacking interactions between the aromatic rings of RB5 and the modified clay surface further stabilize the adsorbed dye molecules (Aromatic π -system (RB5) ... HDTMA-modified surface). Under certain oxidative conditions, hydroxyl radicals ($\bullet\text{OH}$) generated on the modified clay surface can cleave the azo bond ($-\text{N}=\text{N}-$) in RB5, leading to the oxidative degradation of the dye into smaller, less toxic compounds (RB5 ($-\text{N}=\text{N}-$) + $\bullet\text{OH}$ → Amines + Sulfonates). The synergistic effect of these mechanisms strong

electrostatic attraction, hydrophobic interactions, and π - π stacking results in significantly higher adsorption capacities for HDTMA-modified montmorillonite compared to raw montmorillonite.

Regeneration and reusability

In addition to kinetic and isotherm analyses, the reusability of adsorbents is a critical parameter for evaluating their practical applicability in wastewater treatment. A simple adsorption test using RB5 dye was conducted to examine the potential for reusing natural and modified clays. The results showed a slight decrease in the removal rate of approximately 5%. These findings are supported by previous studies that highlight successful regeneration strategies for dye removal. For instance, Vakili et al. (2020) demonstrated that hybrid beads composed of chitosan, activated carbon, and hexadecyl amine maintained high RB5 removal efficiency over multiple regeneration cycles with only minor performance loss. Similarly, Lai et al. (2020) reported that three-dimensional graphene-based structures retained about 90% of their adsorption capacity after at least five cycles, while Umpuch and Fakthaisongdechakul (2024) showed that biocomposite beads of montmorillonite embedded in a gelatin matrix could also be efficiently regenerated, sustaining strong RB5 uptake after repeated reuse. Furthermore, Momina et al. (2018) reviewed various regeneration approaches confirming that clay-based adsorbents,

including montmorillonite, can be effectively regenerated through both chemical and thermal treatments.

Conclusion

This study successfully enhanced the adsorption capacity of natural montmorillonite clays from Germany and Algeria by modifying them with hexadecyltrimethylammonium bromide (HDTMA). The modification significantly improved their ability to remove Reactive Black 5 (RB5) from water. Batch adsorption tests showed that factors like contact time, pH, and initial dye concentration strongly affected the removal efficiency. Equilibrium was reached within 60 min at a pH of 2 and temperature of 25 °C, with initial RB5 concentration of 100 mg/L.

Kinetic data revealed that the adsorption followed a pseudo-second-order model, indicating that chemisorption driven by ionic interactions specifically between the sulfonic groups of RB5 and the quaternary ammonium groups of HDTMA was the main mechanism. Among the isotherm models evaluated, the Langmuir model best fit the data (highest R^2), confirming that adsorption occurred as a monolayer on uniform sites, with maximum adsorption capacities of 113.4 mg/g for Mnt AM and 101.8 mg/g for Mnt GM. The Temkin model provided further insight into adsorption energy distribution and the nature of adsorbent–adsorbate interactions, while the Freundlich model helped describe adsorption on heterogeneous surfaces.

Moreover, Mnt A and Mnt G revealed endothermic and spontaneous behavior with increased randomness at the solid–liquid interface, while Mnt AM and Mnt GM exhibited exothermic and less spontaneous tendencies with decreased randomness, especially at higher temperatures (45–50 °C), as indicated by the ΔH° , ΔG° and ΔS° values.

Overall, these results demonstrate the excellent performance of HDTMA-modified Algerian montmorillonite (Mnt AM), confirming that organoclays are promising, efficient, and sustainable materials for removing dyes in textile wastewater treatment. This approach not only supports environmental protection and water resource sustainability but also has potential for application in removing other toxic pollutants on a larger scale in the future.

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Declarations

Conflict of interest Not applicable.

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